arXiv:cond-mat/0607745v1 [cond-mat.stat-mech] 28 Jul 2006

Ergodicity of the Nosé-Hoover method

Hiroshi Watanabe*

Department of Complex Systems Science, Nagoya University, Nagoya 464-8601, Japan

Hiroto Kobayashi

Department of Natural Science and Mathematics, Chubu University, Kasugai 487-8501, Japan

(*v3.2 released March 2006*)

Ergodicity of the systems with Nosé-Hoover thermostat are studied. The dynamics of the heatbath variables are investigated and they can be periodic when the system has quick oscillation. The periodic behaviour of them causes the system to lose its ergodicity. The kinetic-moments method is also studied, and the heatbath variables in this method are found to be chaotic. The chaotic behaviour makes the whole system ergodic.

Keywords: Nosé-Hoover thermostat, heatbath

1 Introduction

Molecular dynamics (MD) simulations have become more powerful tools with the development in performance of computers. The standard MD simulations have been performed with constant energy, and therefore, these simulations have taken samples in the microcanonical ensemble. It is required to perform constant-temperature MD (1), because the most of physical quantities are observed in constant-temperature environment. Nosé proposed the extended system method which allows to simulate constant-temperature MD conserving time-reversible property (2). Hoover reformulated the Nosé's method to a more practical one, which is now called the Nosé-Hoover method (3).

Recently, the Nosé-Hoover thermostat has been applied not only for the equilibrium system but also for non-equilibrium phenomena. Ogushi *et al.* studied the heat conduction of the three-dimensional Lennard-Jones particle system using molecular dynamics simulation (4). They put two thermostat with different temperatures on the both ends of the system to achieve the spontaneous phase separation.

The Nosé-Hoover method achieves Gibbs' canonical ensemble when the system is ergodic. However, some numerical researches report that the system with a small degree of freedom often loses its ergodicity, and consequently, the system cannot be canonical in Gibbs' sense. In the system studied by Ogushi *et al.*, for instance, the density at the higher-temperature side becomes dilute, and the number of particles controlled by the thermostat can be very small. Therefore, the system can lose the ergodicity.

In order to improve the ergodicity of a system with thermostat, many methods have been proposed (5; 6). However, there are less studies investigating why and how the system loses its ergodicity. In the present article, we focus the ergodicity of some systems in which temperature controlled by the Nosé-Hoover method.

---

*Corresponding author. Email: hwatanabe@is.nagoya-u.ac.jp

2

2 Nosé-Hoover Method

Consider an isolated system described by a Hamiltonian $\mathcal{H}(\mathbf{p}, \mathbf{q})$ with momenta $\mathbf{p}$ and coordinates $\mathbf{q}$. The equations of motion are

$$\dot{q}_i = \frac{\partial \mathcal{H}}{\partial p_i}, \tag{1}$$

$$\dot{p}_i = -\frac{\partial \mathcal{H}}{\partial q_i}, \tag{2}$$

where $\dot{A}$ denotes the differentiation of A with respect to time. The energy of the system is conserved.

Following Nosé and Hoover, we can achieve the canonical ensemble by modifying the equations of motion as follows:

$$\dot{q}_i = \frac{\partial \mathcal{H}}{\partial p_i}, \tag{3}$$

$$\dot{p}_i = -\frac{\partial \mathcal{H}}{\partial q_i} - \zeta p_i, \tag{4}$$

$$\dot{\zeta} = \left(\frac{K}{K_0} - 1 \right) \frac{1}{\tau^2}, \tag{5}$$

$$\dot{\eta} = \zeta, \tag{6}$$

where ζ and η are additional variables expressing the Nosé-Hoover thermostat, and K, K_0, and τ are the kinetic energy, the aimed temperature, and the relaxation time of the thermostat, respectively.

While the system with the Nosé-Hoover thermostat does not have the canonical form, a quantity

$$\mathcal{H}' = \mathcal{H} + K_0(\tau\zeta^2 + 2\eta) \tag{7}$$

is conserved with the original Hamiltonian $\mathcal{H}$. The energy of the system without the thermostat can fluctuate with the Boltzmann weight $\exp(-\beta\mathcal{H})$. Therefore, the system will achieve the canonical ensemble when the system is ergodic.

3 Simulation

In order to investigate the ergodicity of the system with the Nosé-Hoover thermostat, we study the following two systems,

$$\mathcal{H}_{\mathrm{ho}} = \frac{1}{2}(p^2 + q^2), \tag{8}$$

$$\mathcal{H}_{\mathrm{ym}} = \frac{1}{2}(p_1^2 + p_2^2) + \frac{1}{2}q_1^2 q_2^2, \tag{9}$$

where $\mathcal{H}_{\mathrm{ho}}$ and $\mathcal{H}_{\mathrm{ym}}$ are the Hamiltonian of the harmonic oscillator and the Yang-Mills type, respectively.

We performed numerical simulations of the two systems with the Nosé-Hoover thermostat. The time evolution of the systems were calculated by the fourth-order Runge-Kutta method. The time step Δt is set to be 0.005, the aimed temperature K_0 is 0.5, and the total step is 10^7. The results for the harmonic oscillator are shown in Fig. 1. This figure shows that the system loses the ergodicity, and the distribution of the energy is far from that of the canonical ensemble.

The results of the Yang-Mills system are shown in Fig. 2. The phase diagram of (p_1, p_2) is chaotic, and the histogram of the energy shows canonical distribution, while the harmonic-oscillator system does not.
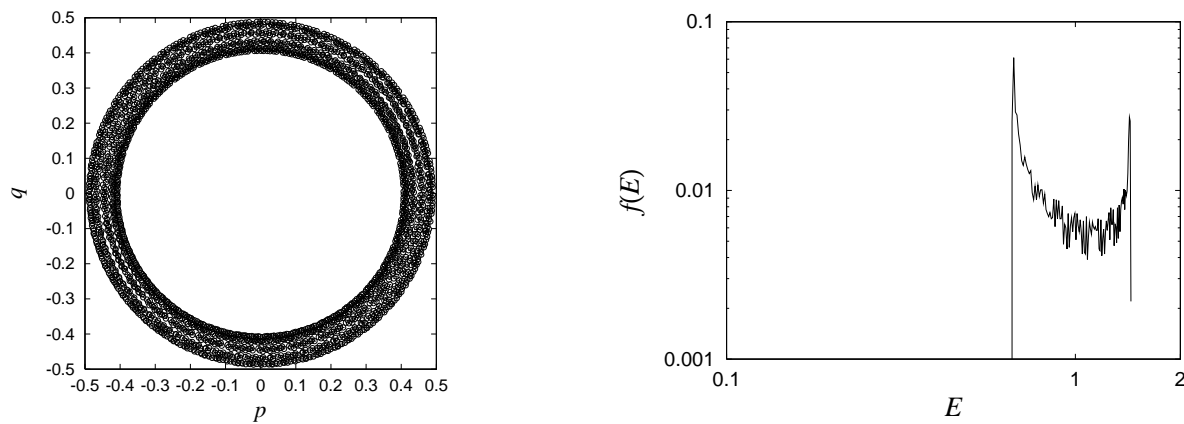
Figure 1. (a) Phase diagram and (b) an energy histogram of the harmonic-oscillator system.
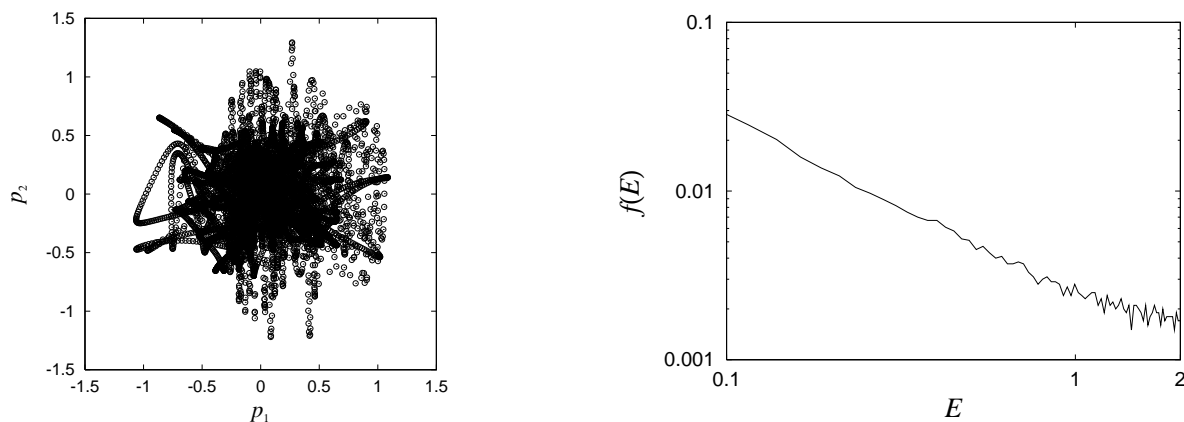

Figure 2. (a) Phase diagram and (b) an energy histogram of the Yang-Mills system.

It suggests that the Yang-Mills system with the Nosé-Hoover thermostat is ergodic while it has only two degrees of freedom.

We focus the dynamics of the heatbath variables in order to figure out why the two systems show different behaviours. The time evolution of the heatbath variables for the harmonic-oscillator system is shown in Fig. 3. The both variables seems to be periodic, and the absolute values of them are bounded throughout the simulations.

The time evolution for the Yang-Mills system is shown in Fig. 4. The behaviour of the heatbath variables seems to be chaotic, and the amplitude is much larger compared to the harmonic-oscillator case. The chaotic behaviour of the heatbath variables is essential for the ergodicity of the system with Nosé-Hoover thermostat.

4   Dynamics of Heatbath variables

In this section, we derive the differential equation for the heatbath variables in order to investigate why the variable show the periodic behaviour in the harmonic-oscillator system. The equations of motion Eqs.(3), (4), and (5) are transformed to be

$$\ddot{\zeta} + 2\dot{\zeta}\zeta + \frac{2}{\tau^2}\zeta = -\frac{1}{K_0\tau^2}pq, \tag{10}$$

in the harmonic-oscillator case.

With large enough τ, the heatbath variable ζ varies much slower than pq. Therefore, we can take an
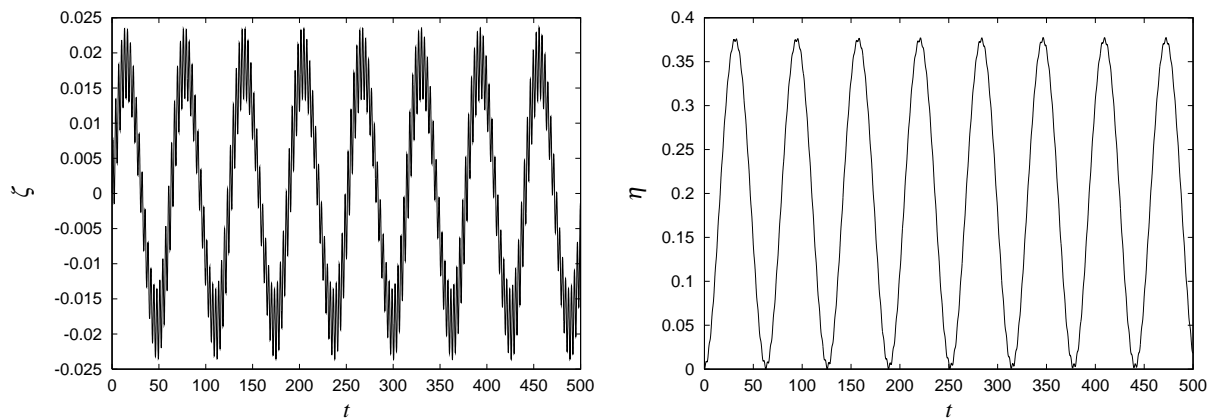
4

Figure 3. The harmonic-oscillator system. Time evolutions of the heatbath variables (a) ζ and (b) η are shown.
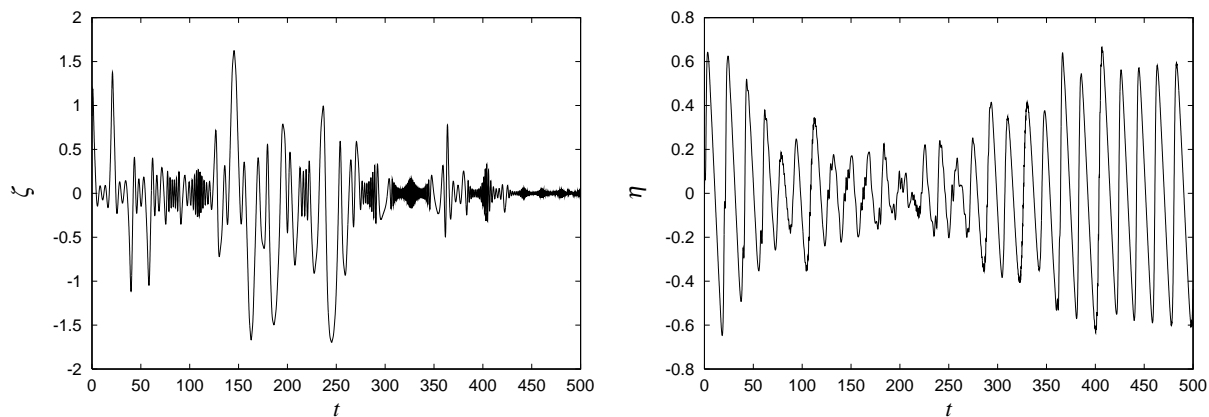

Figure 4. The Yang-Mills system. Time evolutions of the heatbath variables (a) ζ and (b) η are shown.

approximation $\langle pq \rangle = 0$. Assuming the scaling form for ζ to be

$$\zeta(t) = \frac{1}{\tau}\bar{\zeta}(t/\tau), \tag{11}$$

we have the differential equation for $\bar{\zeta}$ to be

$$\ddot{\bar{\zeta}} + 2\dot{\bar{\zeta}}\bar{\zeta} + \bar{\zeta} = 0, \tag{12}$$

which is independent of τ. Therefore, τ-dependence of ζ should have the form in Eq. (11). A quantity

$$H_\zeta = \bar{\zeta}^2 + \dot{\bar{\zeta}} - \log(\dot{\bar{\zeta}} + 1) \tag{13}$$

is conserved in Eq. (12). We can prove that $\bar{\zeta}$ and $\dot{\bar{\zeta}}$ are bounded because of $\dot{\bar{\zeta}} + 1 = K/K_0 > 0$. Therefore, the variable $\bar{\zeta}$ should be periodic. Note that η should also be periodic since $\bar{\zeta}$ is an odd function.

   We solved Eq. (12) numerically using the fourth-order Runge-Kutta method. The initial condition is $\bar{\zeta}|_{t=0} = 0, \dot{\bar{\zeta}}|_{t=0} = 1$. The results are shown in Fig. 5. The behaviour is periodic as expected.

5   Kinetic-Moments Method

Kinetic-moments method is one of the methods proposed to improve the ergodicity even for the harmonic-oscillator case (6). This method controls the kinetic energy $\langle K \rangle$ and its fluctuation $\langle K^2 \rangle - \langle K \rangle^2$ simulta-
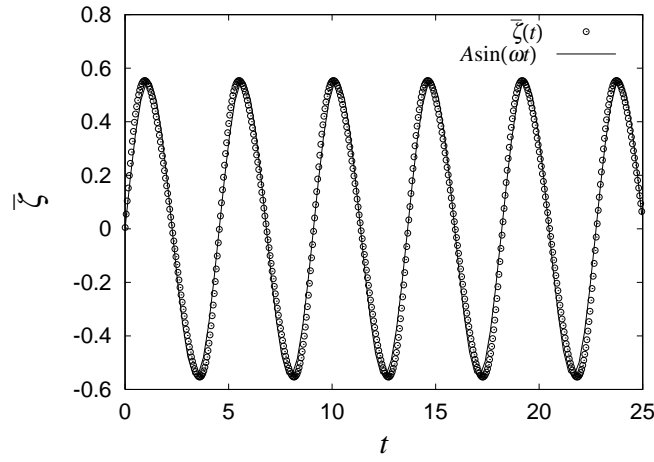
Figure 5.   Time evolution of ζ. The initial condition is $\bar{\zeta}|_{t=0} = 0, \dot{\bar{\zeta}}|_{t=0} = 1$. The behaviour of the heatbath variable is periodic.
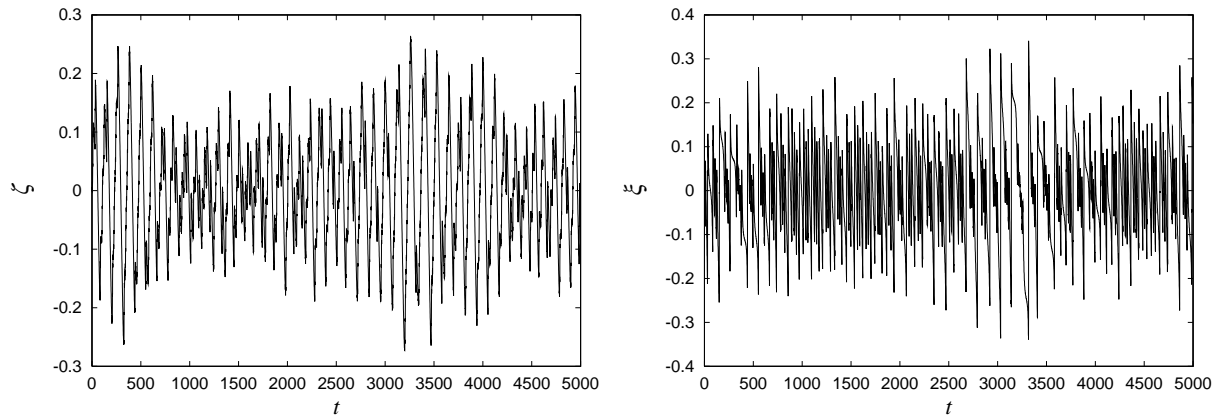

Figure 6.   Time evolutions of the heatbath variables. (a) Time evolution of ζ and (b) that of ξ are shown. The behaviour seem to be chaotic and the amplitudes of the fluctuation are much larger than that of the Nosé-Hoover system.

neously. The equations of motion in this method are

$$\dot{q} = \frac{\partial \mathcal{H}}{\partial p}, \tag{14}$$

$$\dot{p} = -\frac{\partial \mathcal{H}}{\partial q} - \zeta p - \xi p^3, \tag{15}$$

$$\dot{\zeta} = \left(p^2 - 1\right)/\tau_\zeta, \tag{16}$$

$$\dot{\xi} = \left(p^4 - 3p^2\right)/\tau_\xi, \tag{17}$$

with an additional heatbath variable ξ. While Hoover and Holian reported the system with the kinetic-moments thermostat shows good canonical distribution, they did not explain why the method achieves ergodicity.

Here, we discuss the behaviour of the heatbath variables in the method. We simulated the harmonic-oscillator system with the kinetic-moments thermostat. The details of the simulation are same as the previous. The time evolution of the two heatbath variables ζ and ξ are shown in Fig. 6. The heatbath variables seem to be chaotic while the variables are periodic in the Nosé-Hoover system.

We can derive the differential equations for the heatbath variables in the kinetic-moments case. The equations are complex, and are expected not to have any conserved values. Therefore, the kinetic-moments method achieves the ergodicity because of the chaotic behaviour of the heatbath variables, not by controlling higher moments of the kinetic energy.

6   Summary and Discussion

We have studied the ergodicity of the Nosé-Hoover thermostat in the two systems, the one-dimensional harmonic-oscillator and Yang-Mills systems. The numerical results have shown that the Yang-Mills system is ergodic while the harmonic-oscillator system is not.

   In order to study why the two systems have shown the different behaviour, we have derived the differential equation for the heatbath variable. When the system oscillates quickly, the heatbath variable becomes periodic, and consequently the whole system cannot be ergodic. Therefore the Nosé-Hoover system loses its ergodicity not because the system has a small degrees of freedom, but the heatbath variables becomes periodic. A particle system with the Nosé-Hoover thermostat will be ergodic, since quick oscillations are not expected to exist, even if the system has small degrees of freedom. We also explain τ-dependence of the heatbath variable in the amplitude and the period at the same time.

   We have also studied the ergodicity of the kinetic-moments method. This method contains an additional heatbath variables to the Nosé-Hoover method, and it makes the heatbath variables chaotic. The chaotic behaviour of the variables achieves the ergodicity of the whole system. These results imply that at least one of the original system and the heatbath variables should be chaotic in order that the whole system is ergodic.

References

[1] S. Nosé, *Prog. Theor. Phys. Suppl.*, **103**, 1 (1991).
[2] S. Nosé, *Mol. Phys.*, **52**, 255 (1984).
[3] W. G. Hoover, *Phys. Rev. A*, **31**, 1695 (1985).
[4] F. Ogushi, S. Yukawa, and N. Ito, *J. Phys. Soc. Jpn.*, **74**, 827 (2005).
[5] G. J. Martyna, M. L. Klein, and M. Tuckerman, *J. Chem. Phys.*, **97**, 2635 (1992).
[6] W. G. Hoover and B. L. Holian, *Phys. Lett. A*, **211**, 253 (1996).